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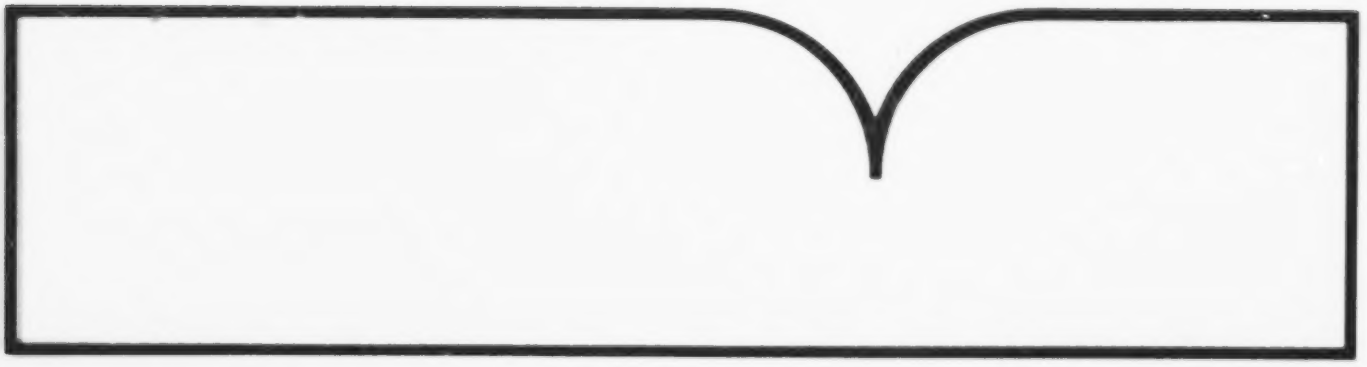

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16. ABSTRACT

On theoretical grounds it is expected that particulate sulfate will deposit more slowly than SO_2. While micrometeorological measurements of the deposition velocity of SO_2 are relatively common, similar simultaneous measurements for sulfate have not been reported. To measure their relative deposition velocities, as well as that of NO_X, a field study was conducted over ungrazed grass in central Ohio in September 1979. Daytime deposition velocities for SO_2 were typically 0.8 cm/sec, while for sulfate typical daytime values were 0.4 cm/sec, which is noticably higher than commonly assumed values. Some late afternoon runs showed a marked decrease in the values. No useful NO_X results are claimed due to substantial variability in the NO_X data.

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AN EXPERIMENTAL STUDY OF SULFUR AND NO_x FLUXES OVER GRASSLAND

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Abstract. Three independent sulfur sensors were used in a study of sulfur eddy fluxes to a field of wheat stubble and mixed grasses, conducted in Southern Ohio in September, 1979. Two of these sensors were modified commercial instruments; one operated with a prefilter to measure gaseous sulfur compounds and the other with a denuder system to provide submicron particulate sulfur data. The third sensor was a prototype system, used to measure total sulfur fluxes. The data obtained indicated that the deposition velocity for gaseous sulfur almost always exceeded that for particulate sulfur; average surface conductances were about 1.0 cm s^{-1} for gaseous sulfur in the daytime and about 0.4 cm s^{-1} for particulate sulfur. The data indicate that nighttime values were probably much lower. The total sulfur sensor provided support for these conclusions. The boundary-layer quantity $\ln(z_0/z_H)$ was found to be 2.75 ± 0.55, in close agreement with expectations and thus providing some assurance that the site was adequate for eddy flux studies. However, fluxes derived using a prototype NO_x sensor were widely scattered, partially as a consequence of sensor noise but also possibly because of the effects of nearby sources of natural nitrogen compounds.

Notation

a	constant
A	proportion of sulfur as gas, $\equiv C_g/C_t$
b	constant
B	normalized conductance, $\equiv V_s/u_*$
C	concentration
$C_{t,g,p}$	concentration; total, gaseous, and particulate
f^*	constant
H	sensible heat flux
T	temperature, or time
$T_{a,s,w}$	temperature; air, surface, and wet bulb.
u	wind speed, horizontal
v_d	deposition velocity
V	signal strength
V_s	surface diffusive conductivity

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$V_{t,g,p}$ surface conductivity; total, gaseous, and particulate
w vertical velocity
z height
z_H roughness length, heat exchange
z_0 roughness length, momentum exchange
θ wind direction
σ standard deviation

1. Introduction

The deposition velocity for sulfate aerosol to natural surfaces remains a somewhat contentious issue. Some workers continue to use the time-honored approximation of about 0.1 cm s^{-1} (e.g., Garland, 1978), on the basis of theoretical and modeling arguments (such as Slim, 1982) and in the absence of convincing experimental evidence to the contrary. Garland and Cox (1982) find that the deposition velocities for particles 0.05–0.2 μm in diameter do not exceed 0.1 cm s^{-1}, on the basis of a limited number of gradient measurements over grass, not sorted by chemical species. However, results for sulfate aerosol appear to be different. In particular Hicks and Wesely (1980) and Hicks *et al.* (1982) present data obtained over a pine plantation, which yield a daytime surface resistance to sulfate transport of about 1.5 s cm^{-1}, indicating that deposition velocities could exceed 0.5 cm s^{-1} in daytime.

There is much more general agreement concerning the deposition of gaseous sulfur, especially sulfur dioxide. Chamberlain (1980) summarized a selection of experimental results that agree on the importance of biological factors. Stomatal aperture, usually seen as a controlling factor, imposes a resistance to uptake that varies much as the stomatal resistance to water vapor transfer. The analysis presented by Wesely and Hicks (1977) took much the same viewpoint, although on more theoretical grounds. Results presented by Garland and Branson (1977), based on cuvette studies of the deposition of radioactively-tagged sulfur dioxide to a pine forest, indicate deposition velocities ranging from 0.1 cm s^{-1} at night to 0.6 cm s^{-1} for a daytime maximum. The canopy in question was similar to that mentioned above in the context of sulfate aerosol deposition. The near equality of deposition velocities for gaseous and particulate sulfur for this type of surface is especially intriguing. While we suspect sulfate aerosol to be less rapidly deposited to vegetated surfaces than gaseous sulfur dioxide, similar velocities appear to apply for the case of some forest canopies. Any such conclusion remains relatively poorly based, since no report has yet been published of simultaneous measurements of the fluxes of gaseous and particulate sulfur compounds to natural surfaces.

Against this background, it was decided to perform a study of gaseous and particulate sulfur eddy fluxes to a land surface, as part of the EPA Ohio River Basin study, during September 1979. Several pollutant sensors were selected for testing, including NO_x and particle detectors. Results obtained using the NO_x and particle instruments were widely scattered. The NO_x data will be used here, however, to illustrate the difficulties that can arise when micrometeorological covariance and/or gradient methods are applied in poor

experimental situations. The objectives of this paper are (a) to describe the system used to measure dry deposition eddy fluxes, (b) to summarize the problems involved with making such measurements and the corrections that must be applied in some circumstances, (c) to present data obtained in a field study of sulfur dioxide, particulate sulfur, and NO_x, and (d) to demonstrate the way in which confidence can be generated in the data obtained.

2. Experimental

2.1. Experimental site

Figure 1 shows the location of the site selected for this study, chosen to be in a region of high ambient sulfate levels, so as to provide concentrations suitable for flame photometric detection, and in relatively flat and spatially homogeneous terrain. The latter requirement proved to be difficult to satisfy, since much of the Ohio River valley is rolling farmland subdivided into plots usually less than 20 ha. Micrometeorological measurement methods require spatial uniformity of surface slope and vegetation for

Fig. 1. A map showing the location of the 1979 field site, near South Charleston, Ohio, and indicating major cities in the area. The hatched wedge indicates the sector of preferred wind directions.

upwind distances (fetches) of the order 100 times the height of meteorological measurement. Typical field applications make use of sensors distributed up to 10 m height, so that fetches of more than one kilometer are usually desired. A suitable field site was located adjacent to the Western Branch of the Ohio Agricultural Research and Development Center (OARDS), near South Charleston, Ohio.

Instrumentation was set up on OARDS land in a location that permitted maximum fetch across adjacent ungrazed grassy surfaces to the south and southeast (Figure 2).

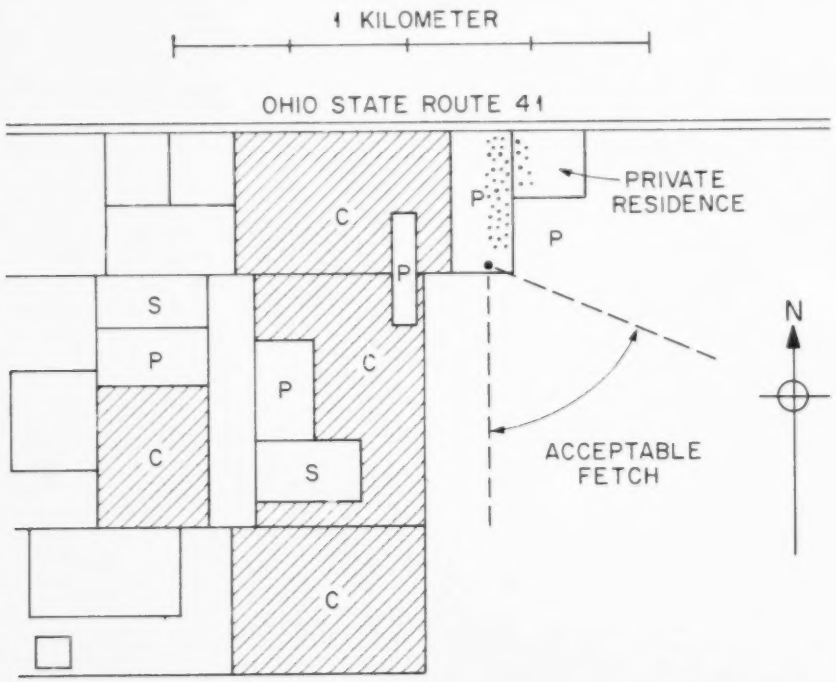

Fig. 2. The layout of fields and crops in the immediate vicinity of the Ohio field site. As in Figure 1, the sector of acceptable wind directions is shown. Fields identified with S were planted with soybeans, C indicates corn (maize), and P ungrazed pasture. Some trees were in the immediate vicinity of the sampling site, as indicated by stippling.

Surface vegetation was uniform for more than one kilometer in these preferred directions, although the elevation decreased slightly towards the south. The tower location (see Figure 3) was nearly at the crest of a slight rise. Since the intent of this study was not to investigate the characteristics of turbulence, but to look for differences between gaseous and particulate sulfur deposition velocities, the site imperfections were viewed with more tolerance than would be usual in micrometeorological work.

2.2. Micrometeorological Equipment

Several micrometeorological techniques are suitable for measuring vertical fluxes of pollutants. The eddy-correlation (or covariance) method was used in the present study, since this provides an absolute measurement of the deposition rate without relying on estimated eddy diffusivities or other inferred quantities.

Turbulence instrumentation was mounted on a boom extending about 2 m upwind of an open scaffolding tower, at 6.5 m height (see Figure 1). Vertical wind speed was measured with a propeller anemometer, horizontal speed with a two-rotor, six-cup anemometer. Temperature fluctuations were measured with a microbead thermistor, operated in a DC bridge driven by about 1 V so as to minimize self-heating.

No attempt was made to arrange for equal time constants of the turbulence sensors employed. Provided sensors have sufficiently fast response, the performance in eddy-correlation applications is governed by the slowest sensor of the set under consideration (usually the chemical detector in an application like this). Sufficient is known about turbulence cospectra and the measurement of fluxes that in many instances corrections for inadequate sensor response can be applied with confidence (e.g., Hicks, 1972); however, it is prudent to arrange matters so that such corrections are not large.

Mixing-length theory dictates that in daytime it is necessary to measure turbulence fluctuations with spatial dimensions similar to the height above the ground. Experience has shown that the use of detectors with distance constants shorter than half the height of operation assures that corresponding corrections for inadequate sensor response characteristics will usually be less than 20% in daytime, convective conditions. Likewise, it is not necessary that the detectors be coincident in space (although this is clearly a desirable goal). In the present experiment, the measurements were obtained in a volume of about 1 m diameter at about 6.5 m height. The errors arising from separation of sensors are also fairly well known (also see Hicks, 1972, for example).

In stably stratified conditions, considerably more stringent constraints apply, in all aspects, because turbulent transfer is at higher frequencies (Kaimal *et al.*, 1972). The present data were obtained only in unstable and near-neutral conditions.

Routine meteorological observations of wind speed and direction, temperature and humidity were made at 7 m, using the same tower. Net radiation was measured at about 2 m above the grass. At infrequent intervals, surface temperatures were measured using a hand-held infrared thermometer, and air temperature and humidity were measured using a ventilated psychrometer at about 1 m height.

2.3. Sulfur Concentration Sensors and Calibration

Two commercial flame photometric sulfur sensors were modified to make them specific for particle and gaseous sulfur*. On the gaseous sulfur unit, a Millipore LSWP teflon filter with a 5 μm pore size was used to provide a particle-free air stream to the sampling device. The other modified system (particulate sulfur) employed a 25 cm long,

* The commercial sulfur sensors were Meloy model 285. This does not constitute an official endorsement or recommendation. Other devices could have worked just as well.

0.48 cm diameter lead dioxide coated denuder tube to remove SO_2 from the sampled air stream. Laboratory tests using SO_2-enriched laboratory air indicated that the denuder removed about 99% of SO_2 from the inlet air. A fresh denuder was installed daily. Downstream of the denuder, ammonia was injected** to minimize the loss of H_2SO_4 by volatilization (Huntzicker *et al.*, 1978). The ammonia injection system of the particulate sulfur sensor resulted in a concentration of about 3 ppb at these modified flow rates.

Sample flow rates through both sensors were increased from 3 to about 7 $cm^3 s^{-1}$, to decrease response and delay times associated with flow through the sampling system. After this modification, the response time of the sensors was about 1 s.

Experience obtained during and after the experiment described here has resulted in a considerable improvement in the sulfur detection apparatus. At the time of this early experiment, modifications were mainly associated with plumbing and with the structure of the burner assembly. For example, the lengths of all air lines were minimized, and the volume of the burner assembly was reduced. Flow rates were increased by removing a constriction in the main sampling line. Later experience has demonstrated the utility of accurate control of all flow rates (both of the sample air stream and of the hydrogen supply for the flame), and has proved the benefit of injecting trace quantities of sulfur hexafluoride into the sampled air stream in order to improve sensitivity.

To avoid interference with flow near the meteorological sensors, the sulfur analyzing apparatus was mounted about 3 m downwind of the anemometers. From a point near the anemometers, air was drawn at high velocity through a 3 m length of 5 cm diameter, teflon coated aluminium tube. Small portions of the air stream were diverted to the sulfur analyzers. Subsequent tests indicated no detectable loss of submicron sulfate aerosol through this sampling system, but effects on particles larger than 2 μm diameter were probably severe.

The third sulfur sensor was a prototype device employing a water-cooled, glass burner assembly**, based on a design reported by Hadjetofi and Wilson (1979). A CO_2-driven venturi exhaust system was used in place of a positive displacement pump to provide a sufficient flow of air through the sensor. Laboratory tests indicated an exponential response time of about 0.3 s, and a sampling delay (lag) time of about 1 s.

Typical air pollution sensors are designed to provide constant calibrations over extended periods, and relatively slowly varying signals. It is sometimes an easy matter to remove those parts of the analyzing equipment that reject high frequency components of the output signal, and to modify the apparatus to decrease the effective time constant, but usually this can be accomplished only at the expense of features that are normally considered essential. Two major difficulties arise when commercial flame photometers are modified in this manner. Drifting calibration is of great concern. In the study described here, instruments were 'warmed up' for several hours before measurements

* The ammonia source was a Metronics 140633021 permeation wafer device. This does not constitute an official endorsement.

** This instrument was developed at the University of Michigan, under the sponsorship of the U.S. Department of Energy.

Fig. 3. A photograph of the 7 m scaffolding tower from which eddy correlation and other meteorological measurements were made. Note the horizontal boom carrying velocity sensors for covariance measurements, the long sampling inlet tube for drawing air samples into the particulate and gaseous sulfur analyzers, and the flexible sampling hoses for the other air chemistry sensors. Equipment was arranged on the tower to minimize the obstruction to wind flow.

were taken, and thereafter calibrations were checked at routine intervals, at least every three hours. Also, large amounts of high-frequency instrumental noise are generated by these instruments. Random noise does not normally present any great problem, since eddy correlation provides an automatic and highly efficient noise-immunity: signals that are not correlated with the vertical velocity do not contribute to the long-term average flux of the material in question. However, very large amounts of noise can substantially increase variability of eddy fluxes computed over fairly short time intervals (Wesely and Hart, 1984). This is discussed more thoroughly later.

The photometers of all flame photometric sensors provide output signals (V) that are

related to the concentration of the detected quantity by a power law relationship:

$$V = a \cdot C^b \tag{1}$$

where a and b are constants that possibly depend on factors such as humidity and CO_2 concentrations. The exponent b is typically in the range 1.5 to 2.0. In many commercial applications, electronic circuits are used to linearize outputs, these circuits being adjusted to fit individual instrument performance characteristics. In the present case, the substantial modifications made in order to achieve the desired fast response adversely affected the linearity of supposedly linearized output signals.

An alternative method of analysis was tested. Since turbulent fluctuations of airborne sulfur concentration are small, flame photometer output voltage fluctuations can be closely approximated as

$$V' = a \cdot b \cdot C' \cdot C^{(b-1)} \tag{2}$$

and products obtained using vertical velocity data will yield

$$\overline{w'V'} \simeq a \cdot b \cdot (\overline{w'C'}) \cdot C^{(b-1)} \tag{3}$$

where primes indicate departures and overbars indicate time averages. It is then appropriate to introduce the familiar deposition velocity $v_d \equiv -(\overline{w'C'})/C$, which leads to the useful relation

$$\overline{w'V'}/V = b \cdot (\overline{w'C'})/C = -b \cdot v_d. \tag{4}$$

Thus, provided the output of the sensing device follows the flame photometer relationship (1), close estimates can be obtained of the deposition velocity without detailed information on the mean concentration level or on the precise calibration of the chemical sensor being used. In the present experiment, the electronic configuration of both the modified commercial and prototype instruments permitted easy application of the simplification represented by Equation (4). Tests conducted with the prototype instrument indicated negligible zero drift and a calibration that appeared to change only once during the course of the field program. The other two devices had zero levels and calibration factors that drifted constantly; data were accepted only when drifts were less than 10% hr^{-1}.

The matter of signal contamination by humidity fluctuations was investigated in a series of laboratory tests conducted previously at the University of Michigan. It was found that the photomultiplier output varied linearly with humidity, for any specific sulfur concentration, but with a negative slope so that apparent deposition velocities could be enhanced in strongly evaporating conditions. Effects of this kind are strongest when pollutant concentrations are low. In the present case, neither $SO_4^=$ nor SO_2 concentrations fell below 17 ppb, and humidity corrections are sufficiently small that they have been ignored.

2.4. Data acquisition and reduction

All data were reduced in real time in order to provide immediate evidence of failures of equipment and/or analysis methods, so that remedial steps could be taken. In

addition, signals were also recorded on digital magnetic tape for subsequent intensive analysis.

Signals were fed to the analyzing equipment via instrumentation amplifiers, with adjustable gain and offset (using precision, multi-turn potentiometers) and with differential inputs to provide improved noise-rejection characteristics. Amplifier gains and offsets were checked every day, using accurate voltage sources producing precise square-wave signals suitable for testing the entire eddy correlation system. The treated signals were fed in parallel to independent analog and digital analyzing systems. The analog circuitry was developed from that presented by Hicks (1970), using four-quadrant analog multipliers, analog integration, and continuous strip-chart recording of the covariances. Smoothed covariances were also digitized and recorded on an independent magnetic tape data acquisition system. Up to six covariances could be handled by the analog system. The digital analyzing apparatus employed a minicomputer, programmed to compute means, variances, and covariances from up to eight input channels. Results were printed at about 30-min intervals.

The analog analyzing system employed a 200 s mean removal circuit, equivalent to a simple R-C filter, which was applied also to the w, u, and T signals prior to computation of covariances with the minicomputer. This technique results in some attenuation of very slow contributions to all eddy fluxes, but provides smoother evaluations of the fluxes than alternative methods.

For the early part of the study, signal outputs of the two modified commercial sulfur instruments were insufficiently amplified before computation of covariances. The fluxes quoted later were measured after the error was detected and corrected; however, it is still possible that the results are underestimated using these two instruments, due to lack of signal strength. The problem did not arise for the total sulfur sensor.

Corrections have been applied for the effects of imperfect sensor response and for the delay (or line lag) incurred in sampling. Table I summarizes the performance characteristics of the meteorological and chemical sensors used in this study. Corrections have

TABLE I

Time constants, lag times, and spatial separations of the input ports of samplers used in the 1979 Ohio deposition study. Anemometer distance constants (in m) are converted to time constants by using the wind speed u (in m s^{-1}).

Sensor	Time constant (s)	Time delay (s)	Distance from w sensor (m)
Vertical velocity	$2.0/u$	0	0
Wind speed	$0.4/u$	0	0.4
Temperature	0.12	0	0.1
Total sulfur	0.33	1.1	0.5
Sulfur dioxide	0.9	1.4	0.5
Particulate sulfate	1.0	1.6	0.5
NO_x	0.15	0.6	0.3

been calculated assuming the stability-dependent spectral shapes of Kaimal *et al.* (1972), using the techniques of Hicks (1972). Most of the corrections are less than 30%. These corrections can be calculated with some confidence. Errors involved in their evaluation should impose less than 5% uncertainty on the final flux determinations.

3. Results

3.1. General

Table II lists the basic meteorological conditions during the three days in which winds were from the acceptable sector indicated in Figures 1 and 2. The times shown correspond to the periods during which eddy fluxes were measured.

Table III presents the pollutant flux data expressed as deposition velocities, after corrections have been applied for the effects of limited sensor response and for spatial separation, as indicated in Table I. Note that the fraction of airborne sulfur present in gaseous form is also tabulated for each experimental run. A few important limitations of the data should be emphasized:

- All of the data presented here were obtained with fetches across pasture. Because of the checkerboard nature of the area, a wind direction sector between 110 and 180 deg was selected as that for which data would be accepted (shown in both Figures 1 and 2).
- Only a limited set of sulfur dioxide and sulfate aerosol data was obtained, because of difficulties associated with amplification prior to eddy-correlation analysis.
- The data for NO_x were obtained using a sampling system with a heated molybdenum catalyst to reduce NO_2 and other reducable nitrogen compounds to NO for subsequent measurement by reaction with an excess of ozone. The measurements thus include the total of NO and NO_2; however, no nitric oxide was detected during this particular experiment. The contribution of HNO_3 is unknown (Huebert, 1983). The temperature of the catalyst precluded a large sensitivity to NH_3.
- The NO_x data are exceedingly scattered. They are tabulated not because they are of great value in their own right, but because they illustrate the large run-to-run scatter usually considered to be evidence of experimental deficiencies.

The analysis that follows combines micrometeorological convention with concepts originating in agricultural meteorology and boundary-layer mass transfer theory. The inverse of an experimentally-determined deposition velocity is the total resistance to transfer of the quantity in question. The aerodynamic component to this resistance that is above the very thin layer of quasi-laminar flow enveloping surface elements is the same for all pollutants, and can be readily evaluated from the micrometeorological data obtained in the present study. The equation and techniques for assessing the effect of atmospheric stability are summarized by Wesely and Hicks (1977). The remaining resistance to transfer can be associated with diffusive transport across the boundary layer in immediate contact with the surface and with a surface non-aerodynamic resistance. For some quantities (e.g., sensible heat), this residual resistance is associated solely with transfer across a diffusive layer next to the surface. In this case, the surface

TABLE II

Meteorological conditions during periods of pollutant eddy flux measurement. Wind speed (u) and direction (θ) were recorded at about 7 m height. Dry-bulb (T_a) and wet-bulb (T_w) temperature were measured at 1 m height, using a hand-held ventilated psychrometer. T_s is the infrared surface temperature. Friction velocity (u_*) and sensible heat (H) are derived from covariances. Temperatures given in brackets are interpolated from measurements not made within the sampling period.

Date and time	u (m s^{-1})	θ (deg)	T_s (C)	T_a (C)	T_w (C)	u_* (m s^{-1})	H (W m^{-2})
17 September							
1105–1130	1.62	110	(24.9)	21.8	16.2	0.24	84
1205–1230	2.10	130	(26.3)	22.7	16.7	0.30	96
1235–1300	1.41	151	(27.0)	23.1	17.0	0.40	100
1305–1330	1.40	122	27.7	23.5	17.2	0.40	93
1505–1530	1.83	119	25.9	23.6	17.6	0.11	51
1535–1600	1.40	121	22.9	23.5	17.0	0.11	19
18 September							
1105–1130	2.17	112	26.2	24.0	19.7	0.43	93
1135–1200	2.37	158	25.9	24.0	–	0.28	98
1205–1230	2.48	137	26.4	24.0	–	0.16	86
1235–1300	2.25	137	(26.2)	23.2	–	0.33	85
1305–1330	2.40	153	(26.1)	22.4	–	0.35	94
1335–1400	2.44	146	25.9	21.5	–	0.42	132
1405–1430	2.29	150	26.0	21.5	–	0.35	94
1435–1500	2.36	149	(25.1)	–	–	0.27	48
1505–1530	2.16	143	(24.2)	–	–	0.38	63
1535–1600	2.73	147	(23.4)	–	–	0.36	6
1605–1630	2.84	161	(22.5)	–	–	0.32	21
1705–1730	2.79	173	21.6	–	–	0.23	−23
1735–1800	2.22	167	(20.7)	–	–	0.17	−21
25 September							
0905–0930	1.60	112	(19.2)	17.3	14.1	0.16	20
1135–1200	1.28	168	(25.0)	21.5	14.9	0.15	88
1205–1230	1.44	132	(25.8)	22.0	15.0	0.15	70
1235–1300	1.34	180	26.5	22.5	15.1	0.15	70
1305–1330	1.29	160	26.9	22.9	15.2	0.16	41
1435–1500	1.57	165	26.5	–	–	0.15	53
1535–1600	1.53	152	21.0	–	–	0.15	22

diffusive resistance (and its inverse, the surface diffusive conductivity, V_s) depend on the friction velocity. The dimensionless quantity V_s/u_* is referred to as the normalized conductance B. This property is related to micrometeorological roughness lengths such as that for momentum transfer (z_0) and for sensible heat (z_H) via $kB^{-1} = \ln(z_0/z_H)$, where k is the von Karman constant. The surface resistance for many trace gases is controlled by stomatal aperture, which in turn is dependent on biological factors, water availability, and insolation. Scaling by u_* is less appropriate in this circumstance.

TABLE III

Deposition velocities for total airborne sulfur, gaseous sulfur (mainly sulfur dioxide), particulate sulfur, and nitrogen oxides, measured during the Ohio 1979 experiment. The quantity A is the fraction of total airborne sulfur that was present in gaseous form.

Date and time		Deposition velocities (cm s^{-1})			
	A	Total sulfur	Gaseous sulfur	Particulate sulfur	NO_x
17 September					
1105–1130	0.61	1.78	–	–	1.07
1205–1230	0.53	1.85	–	–	– 0.71
1235–1300	0.52	1.50	–	–	– 0.70
1305–1330	0.49	0.97	–	–	0.24
1505–1530	0.49	0.65	0.96	0.61	– 0.27
1535–1600	0.51	0.66	1.05	– 0.01	–
18 September					
1105–1130	–	0.11	–	–	0.58
1135–1200	–	–	–	–	0.08
1205–1230	–	–	–	–	– 0.09
1235–1300	–	–	–	–	0.21
1305–1330	–	0.36	–	–	3.30
1335–1400	0.55	1.08	–	–	– 1.50
1405–1430	0.45	0.49	–	–	3.01
1435–1500	0.51	0.55	–	–	2.61
1505–1530	0.50	0.81	–	–	– 3.48
1535–1600	0.49	0.99	–	–	– 0.76
1605–1630	0.44	0.85	–	–	– 0.30
1705–1730	0.42	1.41	–	–	1.11
1735–1800	0.41	1.36	–	–	– 3.16
25 September					
0905–0930	–	–	–	–	–
1135–1200	0.57	0.34	0.58	0.72	0.04
1205–1230	0.55	0.25	0.53	0.44	0.20
1235–1300	0.50	0.28	1.01	0.33	0.33
1305–1330	0.45	0.20	0.52	0.12	– 0.33
1435–1500	0.54	0.33	0.18	0.00	0.98
1535–1600	0.57	0.33	0.34	0.00	– 0.20

3.2. Momentum fluxes and friction velocities

An excellent indicator of site deficiencies, sensor exposure problems, and analytical difficulties is the momentum covariance, $\overline{u'w'}$. The present data set provides three alternative evaluations of $\overline{u'w'}$, all derived from the same set of velocity sensors but using different analytical techniques. The purely digital system offers significantly better accuracy and reliability than the analog systems that were often used in earlier studies of this kind. Figure 4 shows evaluations of $\overline{u'w'}$ obtained using the two other methods plotted against the digitally analyzed results. One of the other systems is purely analog,

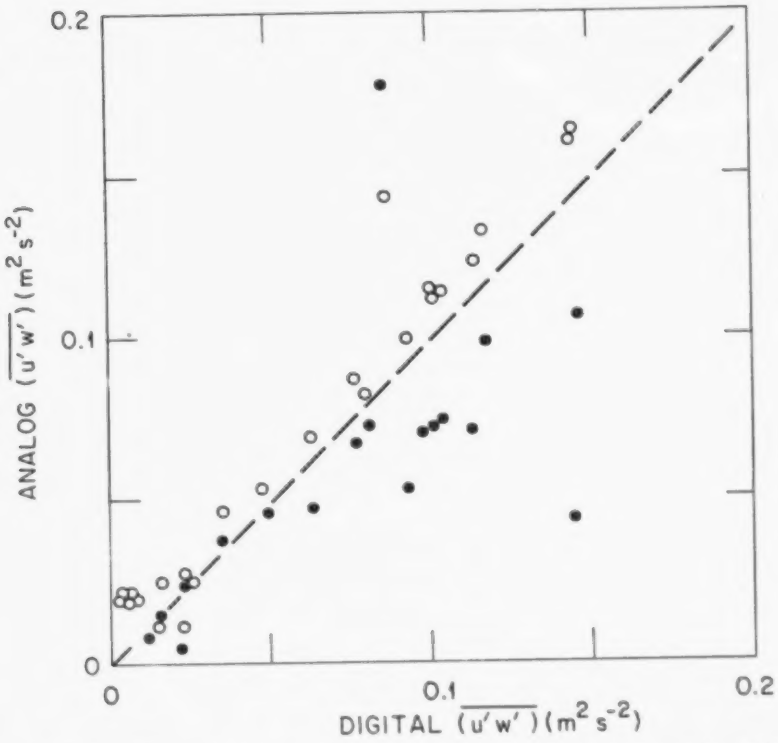

Fig. 4. A comparison between different evaluations of the momentum covariance using analog and digital techniques. Circles indicate the results of analog computations using analog signal averaging and chart recording. Solid circles represent the evaluations yielded by analog signal processing but with digitization immediately after computation of products, with subsequent recording on digital magnetic tape.

producing strip-chart recordings of the smoothed covariances. Figure 4 indicates that the analog evaluations were generally higher than the digital results. Results obtained using a hybrid system with analog analysis to provide instantaneous products but with digital integration and recording seem somewhat more scattered, and underestimate the digital data on the whole. Note that a few outlying values could probably be excluded on statistical grounds; however, for the sake of completeness all measurements have been plotted. The friction velocities listed in Table II are obtained from the averages of the alternative covariance determinations.

Figure 4 provides evidence that the various calibration factors used in these different systems agreed quite well. A further opportunity for examining the data obtained is provided by comparing evaluations of the surface roughness length (z_0) with expectations appropriate for the surface in question, which was made up of stubble with interspersed grassy and broad-leaf plants, typically 0.7 m tall. The mean roughness length derived from the 24 runs with sufficient information in Table II is 9.4 cm with

a standard error corresponding to 38%. Note that the flux-gradient relationships adovated by Dyer (1974) have been used throughout this report, as in earlier analyses (e.g., Wesely and Hicks, 1977).

3.3. Sensible heat fluxes

Figure 5 shows the relationship between the measured covariances $\overline{w'T'}$ and the bulk aerodynamic property $u \cdot (T_s - T_a)$. The ratio of these two independently evaluated quantities determines the bulk aerodynamic exchange coefficient for sensible heat (the Stanton number). The similarity between this plot and graphs of pollutant flux versus concentration is obvious; the Stanton number is basically a dimensionless transfer velocity. It is not possible to draw a single line of proportionality through the data points in Figure 5, because of the wide variability caused by changes in atmospheric stability. (The same would be true for a plot of pollutant flux versus ambient concentration.) It is better to investigate these data analytically after applying corrections for stability as indicated above.

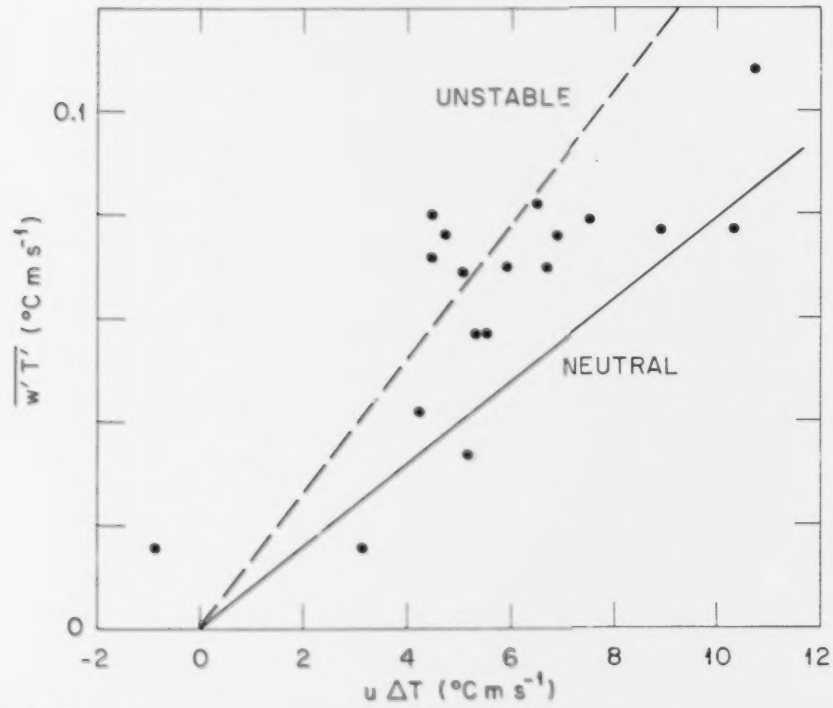

Fig. 5. The relationship between measured sensible heat covariance $\overline{w'T'}$ and the bulk product $u \cdot (T_s - T_a)$. A linear relationship is not expected, since atmospheric stability modifies the bulk transfer coefficient (the Stanton number) considerably. The two lines drawn correspond to near-neutral and moderately unstable stratification.

The average value of the quantity $\ln(z/z_H)$ is 5.04 ± 0.45, with z assumed to be 1 m in this case. Consideration of the momentum roughness lengths derived for this same data set leads to an evaluation of the dimensionless boundary-layer transfer quantity $\ln(z_0/z_H) = kB^{-1} = 2.75 \pm 0.55$ (implying $B \simeq 0.15$). The review of experimental information on boundary-layer transfer relationships by Garratt and Hicks (1973) indicates a value of about 2 for the roughness characteristics of the site used in this study. Thus, the Ohio flux measurements appear to agree with other boundary-layer transfer information, and we can proceed with consideration of pollutant fluxes and deposition velocities with some faith in the experimental procedures.

3.4. Sulfur deposition velocities

Because of the limited quantity of data obtained using the independent gaseous and particulate sulfur sensors, conclusions must be restricted. One conclusion is that sulfate deposition velocities were less than for SO_2 (except on one occasion). A stability-corrected surface conductance analysis yields an average of 1.01 ± 0.26 cm s^{-1} for the gaseous contribution, and 0.35 ± 0.12 cm s^{-1} for the particulate. These evaluations are clearly statistically different, yet must be considered with caution. Also, inspection of the data of Table III reveals evidence of a diurnal variability that might have a substantial influence on the overall average.* Such a diurnal cycle is certainly expected for SO_2, because of the influence of stomatal resistance. The drastic reduction in sulfate deposition velocity and in its surface-layer conductance during the late afternoon is far more evident in the present data, but in this case physiological explanations cannot be offered so easily. If the exceedingly low sulfate deposition velocities recorded in the afternoons are excluded, then the remaining data also indicate slower sulfate deposition than sulfur dioxide: the geometric mean ratio of the surface boundary-layer conductances is $0.48 \pm 48\%$ (from only five values).

There is too much uncertainty in the present evaluations, and too few of them to warrant a more detailed analysis, such as to study in detail the adequacy of normalizing boundary-layer conductance by the friction velocity or to investigate the importance of stomatal resistance. Thus, we shall proceed on the assumption that the surface resistance to transport of SO_2 (the inverse of the conductances already discussed) is about 40% of that appropriate for particulate sulfur. For SO_2 in the conditions of this particular experiment, the surface resistance appears to be about 1.0 s cm, which is much as would be expected on the basis of stomatal resistance arguments (Chamberlain, 1980). We might note that normalizing by the friction velocity and analyzing according to flat-plate boundary-layer transfer theory fails to reduce the variance of the data.

It should be noted that the deposition velocities analyzed here are uncorrected for contributions due to Stefan flow. The errors involved are less than 0.01 cm s^{-1} in the deposition velocity (corresponding to a latent heat flux of 200 W m^{-1}). Effects of thermophoresis and diffusiophoresis are even smaller.

* Furthermore, recent work has indicated that some trace gases might have influenced the 'particulate' data, if they were present (see Durham *et al.*, 1984).

The measurements made using the total sulfur apparatus can be used to investigate whether particulate sulfur was deposited more slowly than was gaseous sulfur. If C_t is the surface concentration of total sulfur, C_g that of gaseous, and C_p that of particulate, then clearly

$$C_t = C_g + C_p. \tag{5}$$

Further, since the surface fluxes are also additive, a second relationship can be written involving the corresponding surface conductances, V_t, V_g, and V_p:

$$V_t \cdot C_t = V_g \cdot C_g + V_p \cdot C_p. \tag{6}$$

In principle, if C_g and C_p vary while V_g and V_p remain fairly constant, the measurements of V_t, C_g, and C_p can be used to infer the average values of V_g and V_p. By combining (5) and (6) we obtain

$$V_t = V_p + A \cdot (V_g - V_p) \tag{7}$$

where A is the proportion of sulfur that is present in gaseous form, as listed in Table III. Note that the quantity A in (7) is the value appropriate very near the surface, whereas evaluations at 6.5 m are given in Table III. The difference will not be great unless the surface resistances of the gaseous and particulate components are substantially different, which does not appear to be the case here.

The data are too widely scattered to enable average values of V_g and V_p to be obtained from (7) by regression of V_t on A. However, the correlation coefficient between V_t and A is statistically different from zero at the 95% level (0.35, from 18 data pairs). The finding of a positive correlation indicates that V_g probably exceeds V_p for these data as well as for the independent observations discussed earlier.

3.5. NO_x FLUXES

Wesely *et al.* (1982) have presented results from an earlier experiment using the same NO_x detector as was used in this study. Unfortunately, the present data display much greater scatter in terms of deposition velocity, which is due at least in part to greater noise in the signal provided by the NO_x measurement system. As shown by Wesely and Hart (1983), the variability expressed as the standard deviation σ_d in deposition velocity can be written as

$$\sigma_d = \sigma_w \sigma_C \bar{C}^{-1} (f^* T \bar{u}/z)^{-1/2}, \tag{8}$$

where σ_w is the standard deviation of the w signal, σ_c is the standard deviation of the C (NO_x concentration) signal, $\bar{C}$ the mean concentration, f^* a constant normally equal to about 5 for the NO_x sensor contaminated with white noise limited to frequencies less than 10 Hz and sampled at a rate of 20 s^{-1}, T the total sampling time (1500 s in this use), $\bar{u}$ the mean wind velocity, and z the height above the ground. For September 18 and 25, σ_d derived from (8) has a value of about 5 cm s^{-1}, larger than the value of 1.7 cm s^{-1} for the 19 values listed in Table III. This discrepancy is perhaps due to the assumption regarding the value of f^* in (8). Noise characteristics on this occasion may have been atypical.

On September 17, the values of measured σ_d seem to have been only a factor of two greater than was the case for the data reported earlier (Wesely *et al.*, 1982; Wesely and Hart, 1983). When (8) is evaluated, $\sigma_d \approx 0.4$ cm s^{-1} is obtained. This is twice the value in the earlier study but is less than the value that can be computed from the very few samples shown for September 17 in Table III.

There is the additional possibility that local surface sources might have affected the measurements of v_d. In particular, the site was located in a grazing area, adjacent to an active pig feedlot, and such areas can contain sources of NO and NO_2 (e.g., see review by Logan, 1983).

The 23 determinations of NO_2 deposition velocity (actually NO_x, but no NO was detected) yield an average, stability-corrected surface resistance of 0.82 ± 1.45 s cm^{-1}. If outlying values (outside bounds corresponding to $\pm$ three standard errors) are excluded, the remaining 17 values yield an average of 0.40 ± 0.58 s cm^{-1}. The process of rejecting outliers can be repeated several times, with little gain in confidence. We might conclude, however, that there is no reason to disagree with the finding of Wesely *et al.* (1982) that NO_2 surface resistance is of the order of 1 s cm^{-1}, and is likely to be largely associated with stomatal resistance is daytime.

4. Conclusions

Measurements of eddy fluxes of momentum and sensible heat made over a large field of ungrazed grassland confirm the surface exchange features documented by Garratt and Hicks (1973), with a dimensionless surface conductance to sensible heat transfer of about $B = 0.15$. Thus, the surface conductance to heat transfer is about 15% of the friction velocity in this circumstance.

Sulfur dioxide and sulfate particle flux measurements indicate deposition velocities for gaseous sulfur generally larger than for particulate. Surface-layer conductances are found to be 1.0 and about 0.4 cm s^{-1}, respectively, in unstable, daytime conditions; corresponding surface resistances are the inverse of these values.

Eddy fluxes of total sulfur measured with a separate sulfur sensor confirm that gaseous sulfur was deposited more rapidly than particulate, but these data are too scattered to permit a detailed examination of the difference.

There is some evidence that sulfate aerosol conductances decrease significantly in the late afternoon. Presumably this low conductance would prevail throughout the night (unless affected by dewfall or some other factor not considered here). Daily average deposition velocities appropriate for SO_2 and sulfate particle deposition to lush grassland can be estimated from these results. As a first estimate, a value of 1 s cm^{-1} for daytime surface resistance to SO_2 deposition and an aerodynamic resistance typically 0.3 s cm^{-1} over grassland suggest a daytime deposition velocity about 0.8 cm s^{-1}. At night, a much slower deposition would be expected.

For particulate sulfate, a daytime deposition velocity of about 0.4 cm s^{-1} is indicated. Again, much lower values would be expected at night. In comparison, we might note the experimental finding of somewhat larger daytime sulfate deposition velocities above

a pine plantation (Hicks and Wesely, 1980; Hicks *et al.*, 1982), and the familiar value of 0.1 cm s^{-1} for sulfate that is used as a time average in many numerical models.

Finally, NO_x deposition velocities were so scattered that little new information can be derived from them. Much of the scatter seems to be related to excessive noise generated during most of the experiment by the NO_x measurement system. Some of the scatter is also likely to be associated with farming practices in the area around the site. A nearby pig feedlot could have generated sufficient nitrogenous emissions to destroy the spatial uniformity of sources and sinks that is required in order for micrometeorological covariance and gradient methods to work well.

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References

Chamberlain, A. C.: 1980, 'Dry Deposition of Sulfur Dioxide', in D. S. Shriner, C. R. Richmond, and S. E. Lindberg (eds.), *Atmospheric Sulfur Deposition*, Ann Arbor Science, Ann Arbor, Michigan, pp. 185–197.

Durham, J. L., Spiller, L. L., Eatough, D. J., and Hansen, L. D.: 1984, 'Dimethyl and Methyl Hydrogen Sulfate in the Atmosphere', in V. P. Aneja (ed.), *Proceedings, Conference on Environmental Impact of Natural Emissions*, Air Pollution Control Association, pp. 263–274.

Dyer, A. J.: 1974, 'A Review of Flux-Profile Relationships', *Boundary-Layer Meteorol.* **7**, 363–372.

Garland, J. A.: 1978, 'Dry and Wet Removal of Sulfur from the Atmosphere', *Atmos. Environ.* **12**, 349–362.

Garland, J. A. and Cox, L. C.: 1982, 'Deposition of Small Particles to Grass', *Atmos. Environ.* **16**, 2699–2702.

Garland, J. A. and Branson, J. R.: 1977, 'The Deposition of Sulfur Dioxide to Pine Forest Assessed by a Radioactive Tracer Method', *Tellus* **29**, 445–454.

Garratt, J. R. and Hicks, B. B.: 1973, 'Momentum, Heat and Water Vapour Transfer to and from Natural and Artificial Surfaces', *Quart. J. Roy. Meteorol. Soc.* **99**, 680–687.

Hadjetofi, A. and Wilson, M. J. G.: 1979, 'Fast-Response Measurements of Air Pollution', *Atmos. Environ.* **13**, 755–760.

Hicks, B. B.: 1970, 'The Measurement of Atmospheric Fluxes Near the Surface: A Generalized Approach', *J. Appl. Meteorol.* **9**, 386–388.

Hicks, B. B.: 1972, 'Propeller Anemometers as Sensors of Atmospheric Turbulence', *Boundary-Layer Meteorol.* **3**, 214–228.

Hicks, B. B. and Wesely, M. L.: 1980, 'Turbulent Transfer Processes to a Surface and Interaction with Vegetation', in D. S. Shriner, C. R. Richmond, and S. E. Lindberg, eds., *Atmospheric Sulfur Deposition*, Ann Arbor Science, Ann Arbor, Michigan, pp. 199–207.

Hicks, B. B., Wesely, M. L., Durham, J. L., and Brown, M. A : 1982, 'Some Direct Measurements of Atmospheric Sulfur Fluxes over a Pine Plantation', *Atmos. Environ.* 2899–2903.

Huebert, B. J.: 1983, Discussion on 'An Eddy-Correlation Measurement of NO_2 Flux to Vegetation and Comparison to O_3 Flux', *Atmos. Environ.* **17**, 1600.

Huntzicker, J. J., Hoffman, R. S., and Ling, C.: 1978, 'Continuous Measurement and Speciation of Sulfur-Containing Aerosols by Flame Photometry', *Atmos. Environ.* **12**, 83–88.

Kaimal, J. C., Wyngaard, J. C., Izumi, Y., and Coté, O. R.: 1972, 'Spectral Characteristics of Surface-Layer Turbulence', *Quart. J. Roy. Meteorol. Soc.* **98**, 563–589.

Logan, J. A.: 1983, 'Nitrogen Oxides in the Troposphere: Global and Regional Budgets', *J. Geophys. Res.* **88**, 10 785–10 807.

Slinn, W. G. N.: 1982: 'Predictions for Particle Deposition to Vegetative Canopies', *Atmos. Environ.* **16**, 1785–1794.

Wesely, M. L. and Hicks, B. B.: 1977, 'Some Factors that Affect the Deposition Rates of Sulfur Dioxide and Similar Gases on Vegetation', *J. Air Poll. Contr. Assoc.* **27**, 1110–1116.

Wesely, M. L. and Hart, R. L.: 1983, 'Variability of Short-Term Eddy-Correlation Estimates of Mass Exchange', in B. A. Hutchison, B. B. Hicks, L. W. Gray, K. L. Parttu, and J. B. Stewart (eds.), *Forest Environmental Measurements Conference Proceedings*, D. Reidel Publ. Co., Dordrecht, Holland (in press).

Wesely, M. L., Eastman, J. A., Stedman, D. H., and Yalvac, E. D.: 1982, 'An Eddy-Correlation Measurement of NO_2 Flux to Vegetation and Comparison to O_3 Flux', *Atmos. Environ.* **16**, 815–820.

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